Characterization of CaO^+ and BaO^+ by Two-Photon Ionization Spectroscopy

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Why are we doing this?

BaO has been studied.

- Plenty of work has been done experimentally
  - Several studies [1, 2, 3] exist studying the chemiluminescence of reactions of the form,

$$Ba + N_xO_y \rightarrow BaO^* + N_xO_{y-1}$$

  - Constants are reported from these studies with very high precision
  - A synchrotron PES of BaO has recorded[4] the IP at 6.46(7) eV

- Not much work has been done theoretically
  - Typically included in papers to supplement experimental work [4]

1. RW Field *et al., J. Chem. Phys* . (1973)
2. Hedderith & Blom, *J. Mol. Spec.* (1990)
3. P. Bernath *et al., J. Chem. Phys.* (2005)
4. J. Dyke *et al., J. Phys. Chem. A* (1987)

Why are we doing this?

BaO has been studied.

- None of the studies of BaO have been below 100 K
  - Our spectra are jet-cooled to < 50 K
- The IP error margin is on the order of hundreds of wavenumbers
  - The value is suspect due to possible ionization from hot states
  - Our error margin is on the order of wavenumbers
- No experimental work exists on the electronic structure of BaO^+
  - Once we find the IP, we can analyze the rovibronic structure with PFI-ZEKE
- Refining this information for the molecular ion is an important step towards a greater degree of control in molecular ion trapping experiments

Why are we doing this?

CaO has been studied.

- Some work has been done experimentally
  - Emission studies were done with a Ca hollow cathode source [5]
  - A synchrotron PES of CaO has recorded the IP at 7.6(5) eV [6]
  - Results from a guided ion beam study indirectly determined the IP at 6.66(18) eV [7]
- Plenty of work has been done theoretically
  - Harrison et. al.[8] did an RCCSD(T) examination of MX (M = Ca, Zn; X= O, F) and predicted many properties
  - Studies have been done up to the MRCI+Q [9] level

5. A. Lagerqvist *et al., Proc. Phys. Soc.* (1950)
6. E. Murad, *J. Chem. Phys.* (1983)
7. NF Dalleska & PB Armentrout, *Int. J. Mass Spec* (1994)
8. JF Harrison *et al., ACS Symposium Series* (2002)
9. H Khalil *et al., J. Phys. Chem. A* (2013)

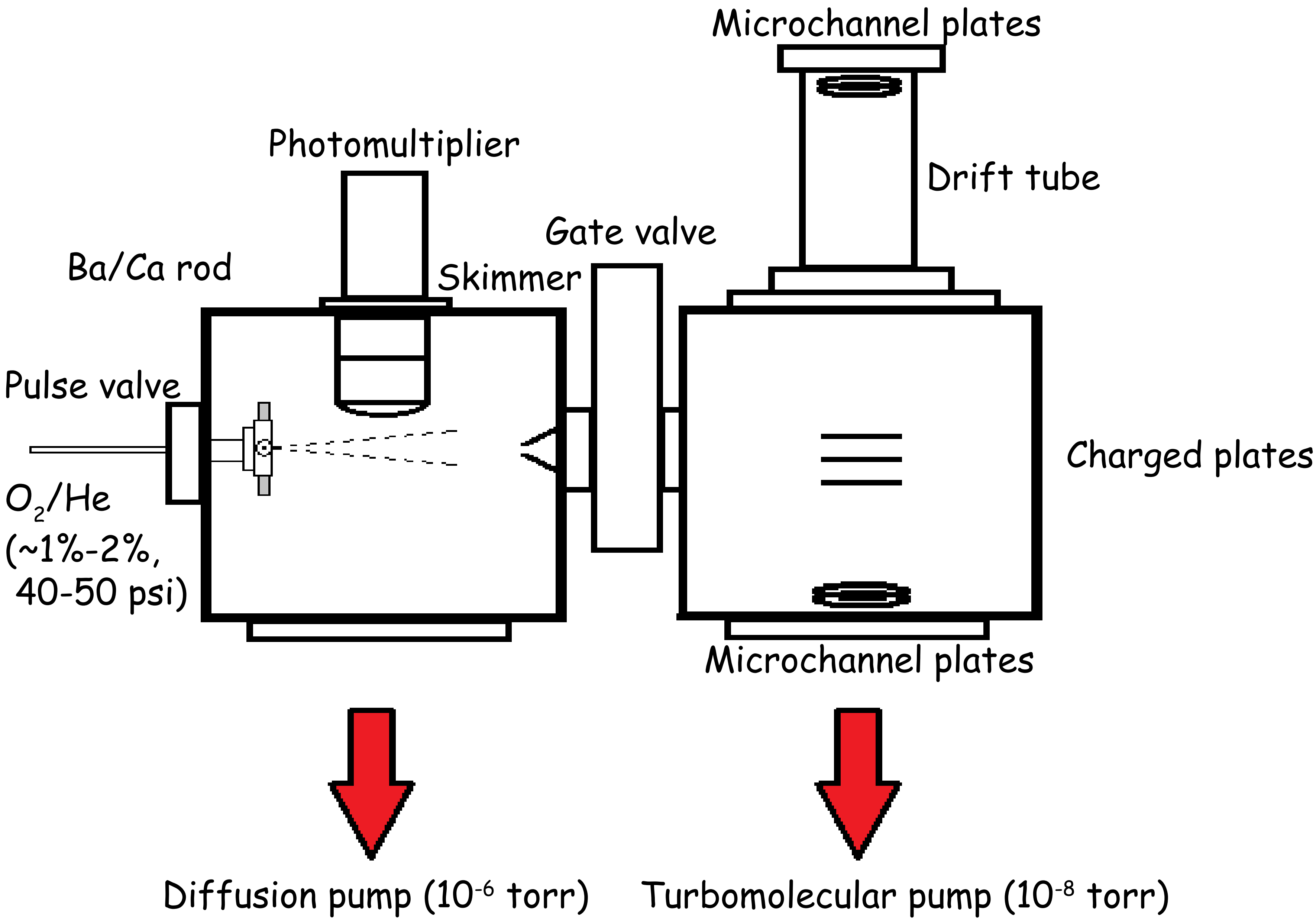
Why are we doing this?

CaO has been studied.

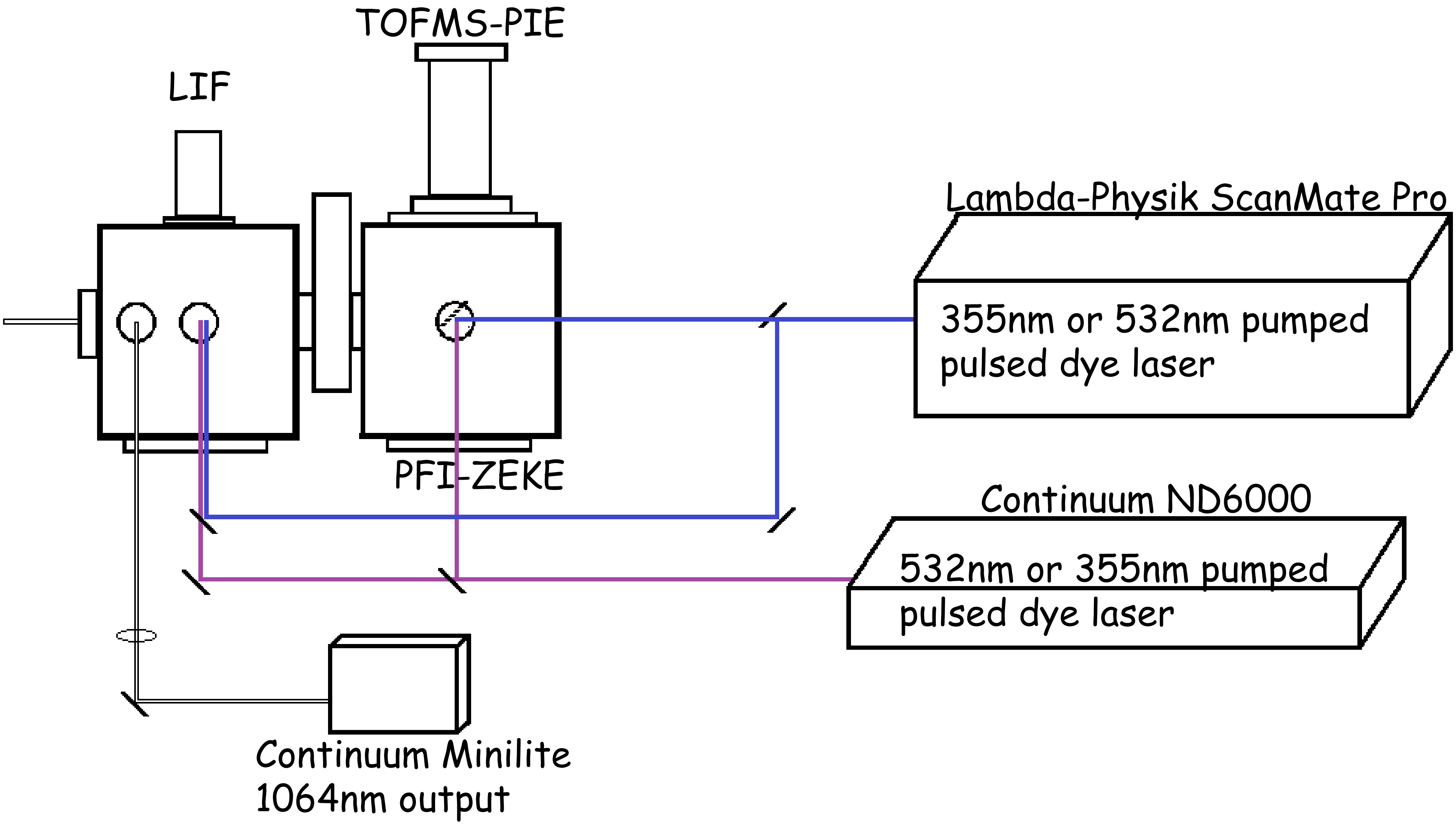
- Previous experimental studies are at high temperature
    - Our jet-cooled apparatus provides advantages
- CaO^+ is an interesting molecule
    - The ground state is $^2\Pi$ with a low-lying $^2\Sigma^+$ state [8, 9]
    - The IP discrepancy can be laid to rest
    - Only theoretical work exists on the electronic structure so far
- Like BaO, CaO is a molecule that can be produced easily after atomic ion trapping in Coulomb crystals, and has potential for further study; knowledge of the quantum states is useful

8. JF Harrison *et al., ACS Symposium Series* (2002)
9. H Khalil *et al., J. Phys. Chem. A* (2013)

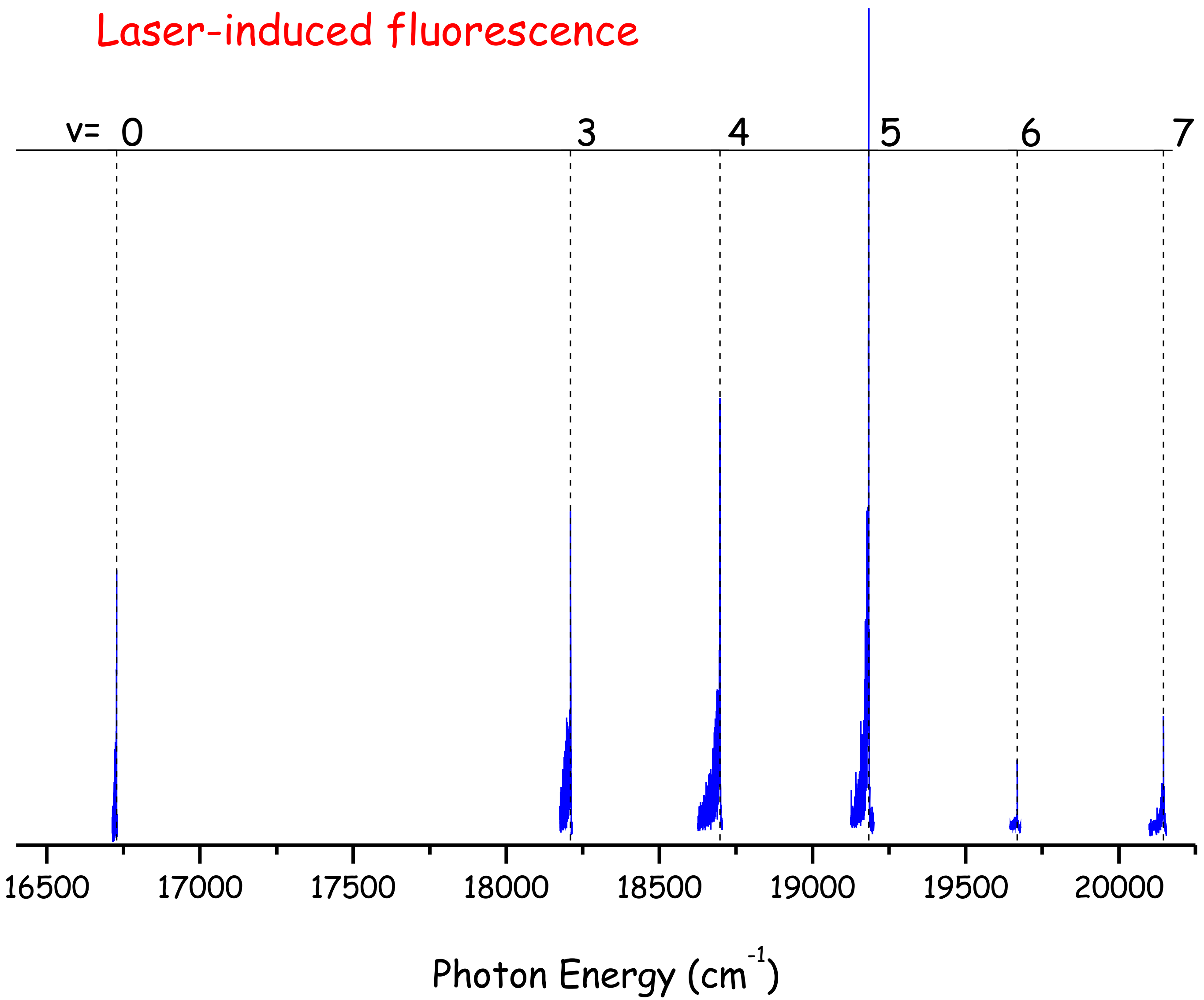
Experimental Setup for jet-cooled metal oxides



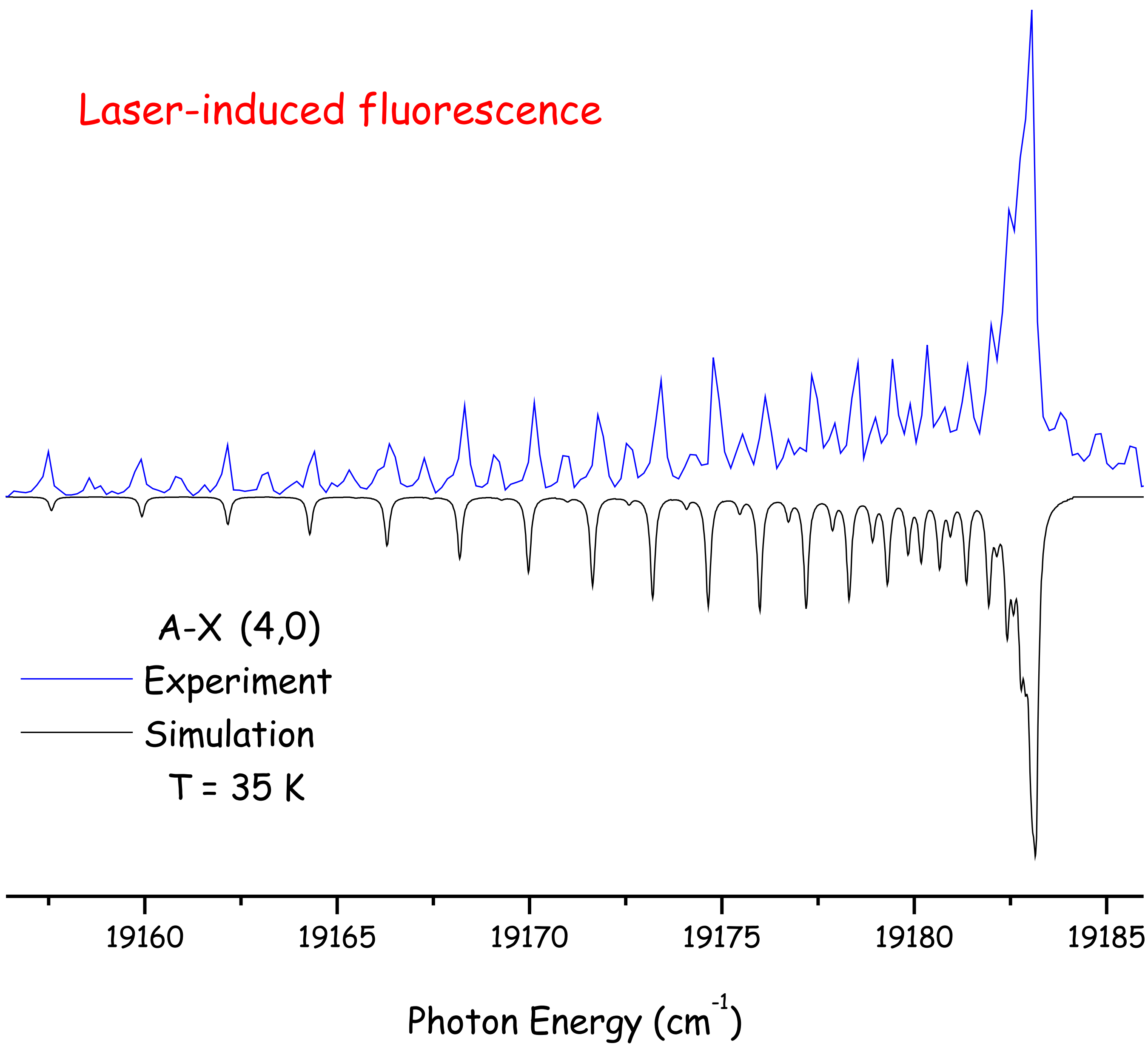
Experimental Setup: Nd:YAG lasers everywhere



BaO $A^1\Sigma^+ \leftarrow X^1\Sigma^+$



BaO $A^1\Sigma^+ \leftarrow X^1\Sigma^+$



$B'' = 0.312614$ cm^{-1}
$B' = 0.271195$ cm^{-1}

CM Western, pgopher, University of Bristol, 2007

BaO $A^1\Sigma^+ \leftarrow X^1\Sigma^+$

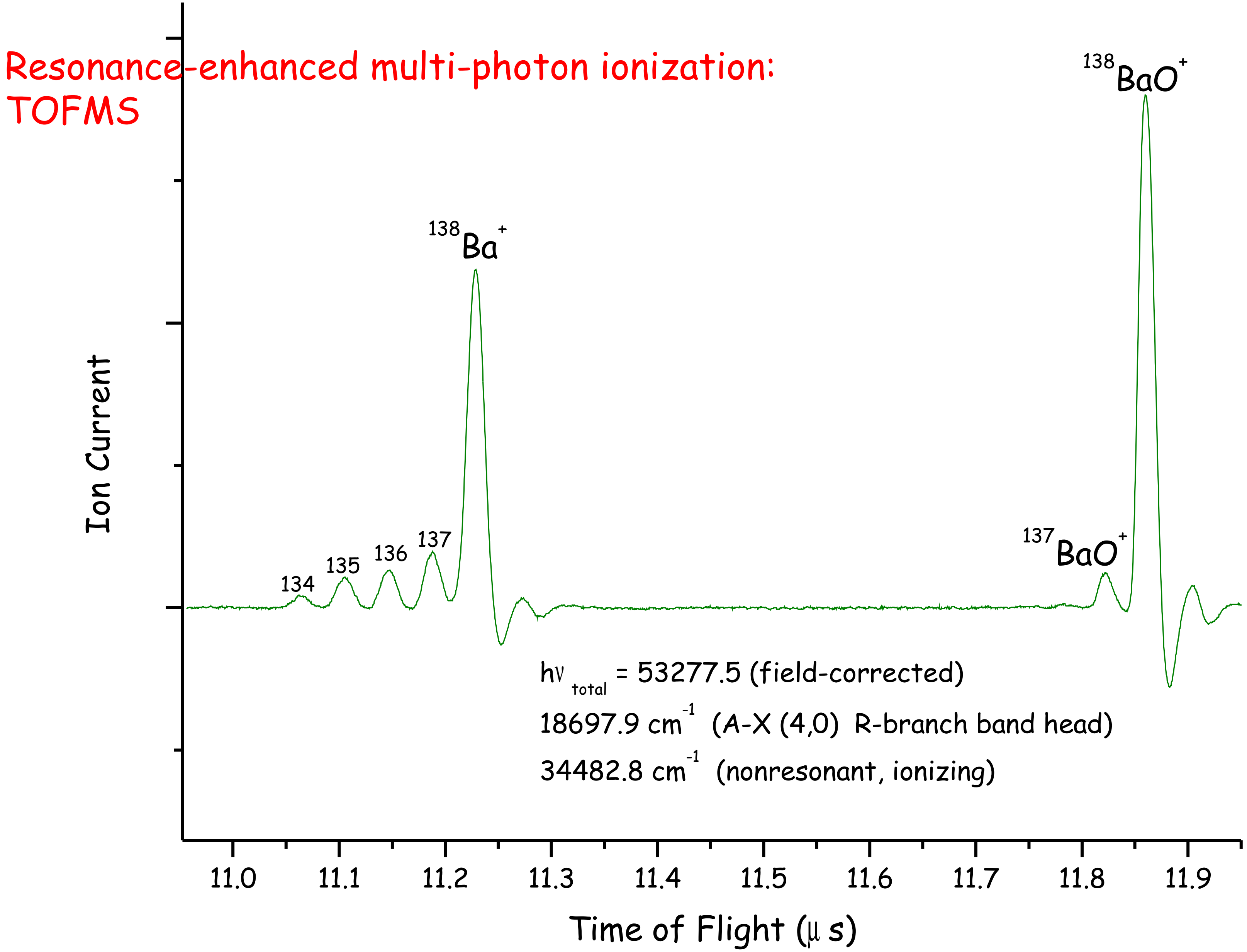
Laser-induced fluorescence

Molecular constants obtained from fit parameters

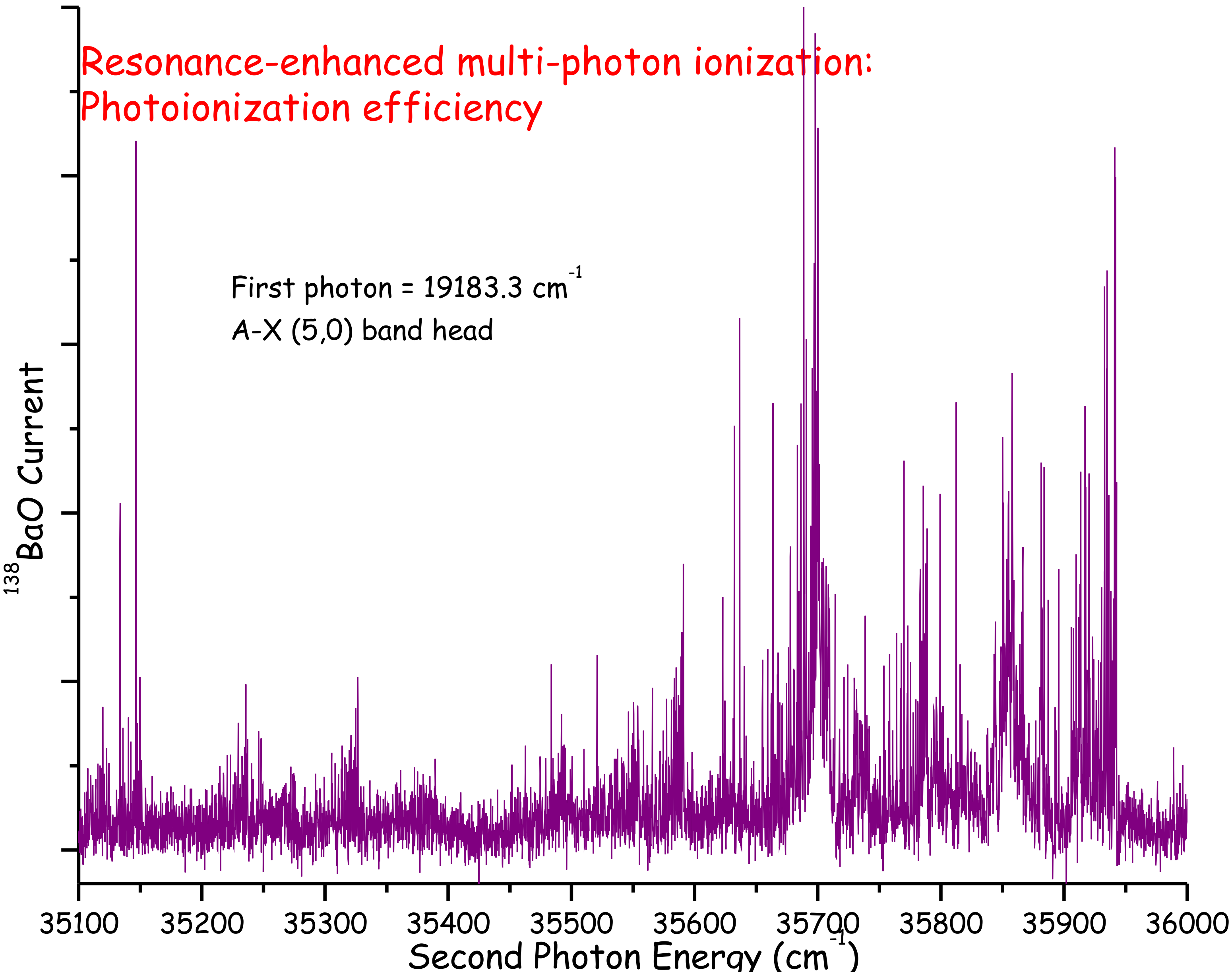
State	Constant	Energy
$X^1\Sigma^+$		0 cm^{-1}
	B_e	0.313 cm^{-1} [3]
	ω_e	669.74 cm^{-1} [3]
	$\omega_e x_e$	2.019 cm^{-1} [3]
$A^1\Sigma^+$		16722.25 cm^{-1} [3]
	$B_{0,3,4,5,6,7}$	0.258[3], 0.255(3), 0.271(3), 0.271(3), 0.269(3), 0.256(3)cm^{-1}
	ω_e	499.5(9) cm^{-1}
	$\omega_e x_e$	1.4(1) cm^{-1}

3. P. Bernath *et al.*, *J. Chem. Phys.* (2005)

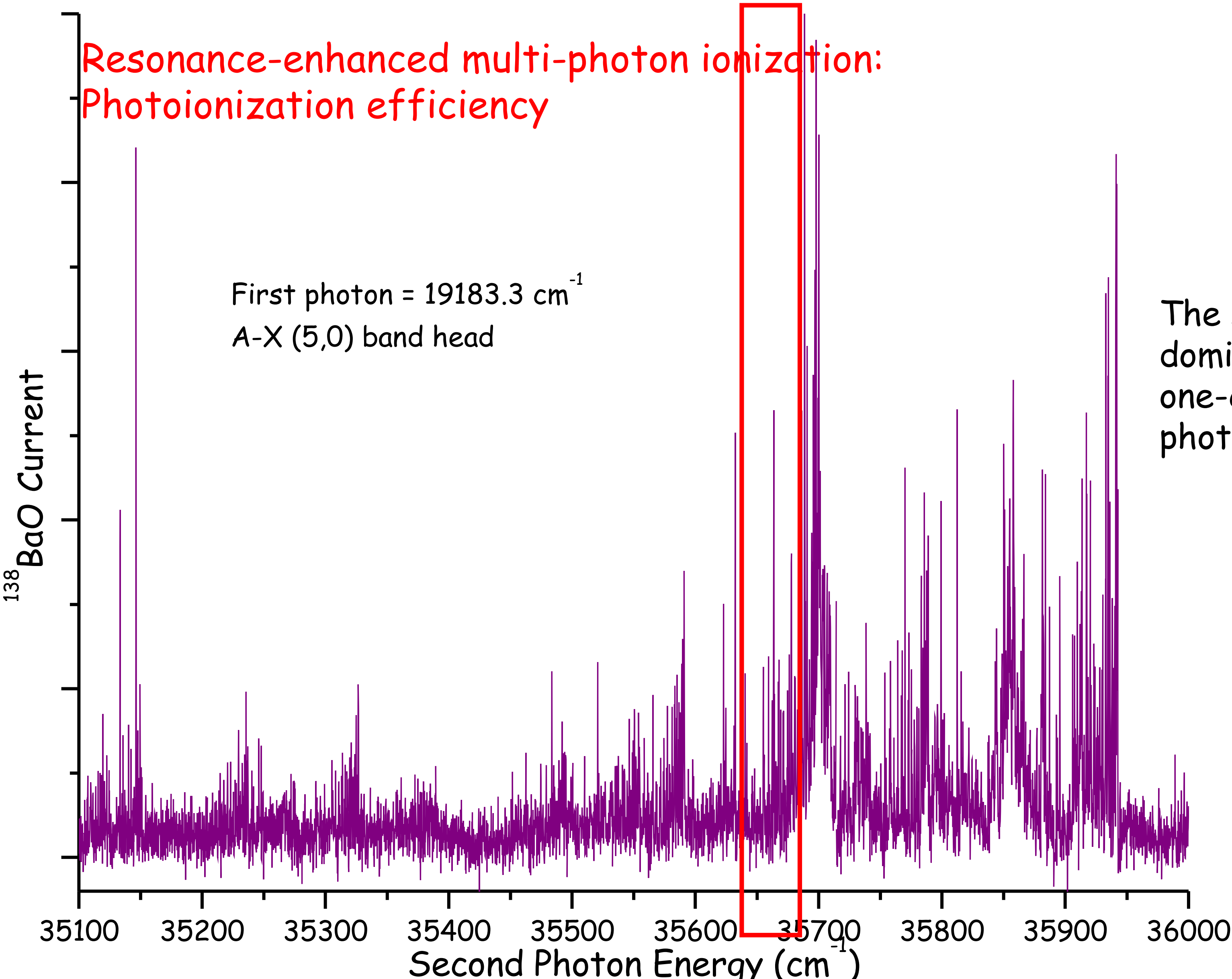
Ionizing BaO



Ionizing BaO

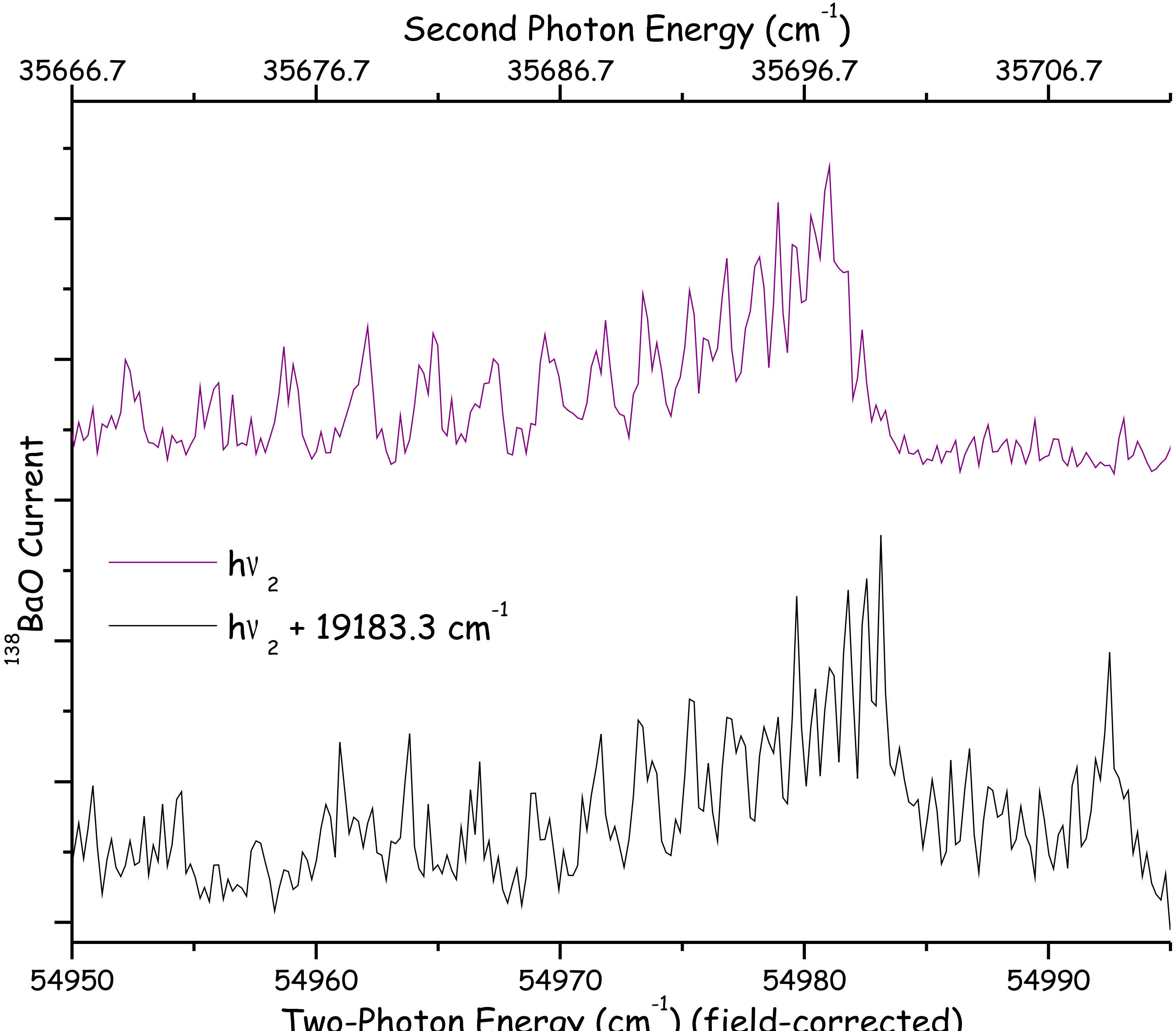


Ionizing BaO

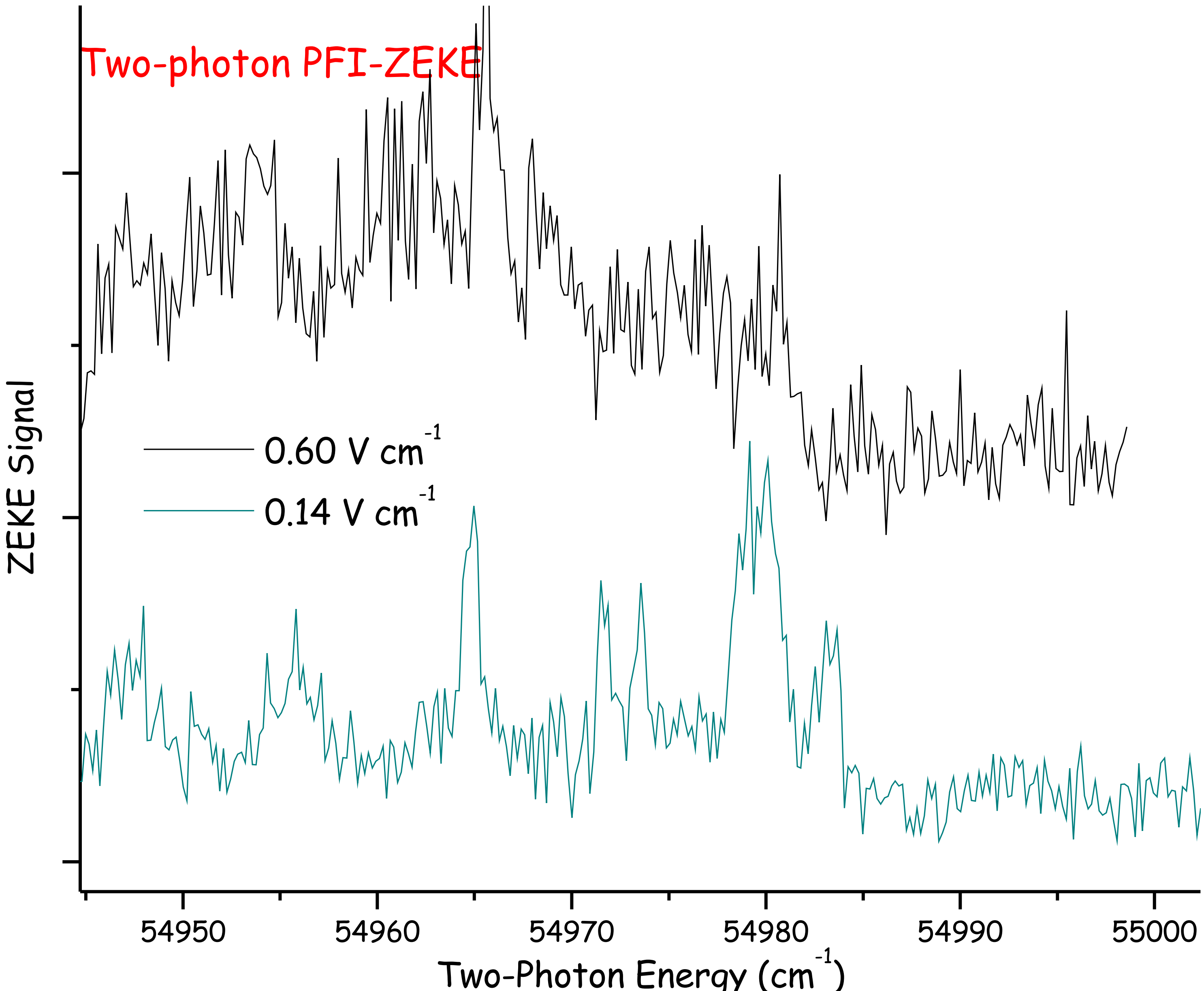


The spectrum is dominated by one-color two-photon ionization!

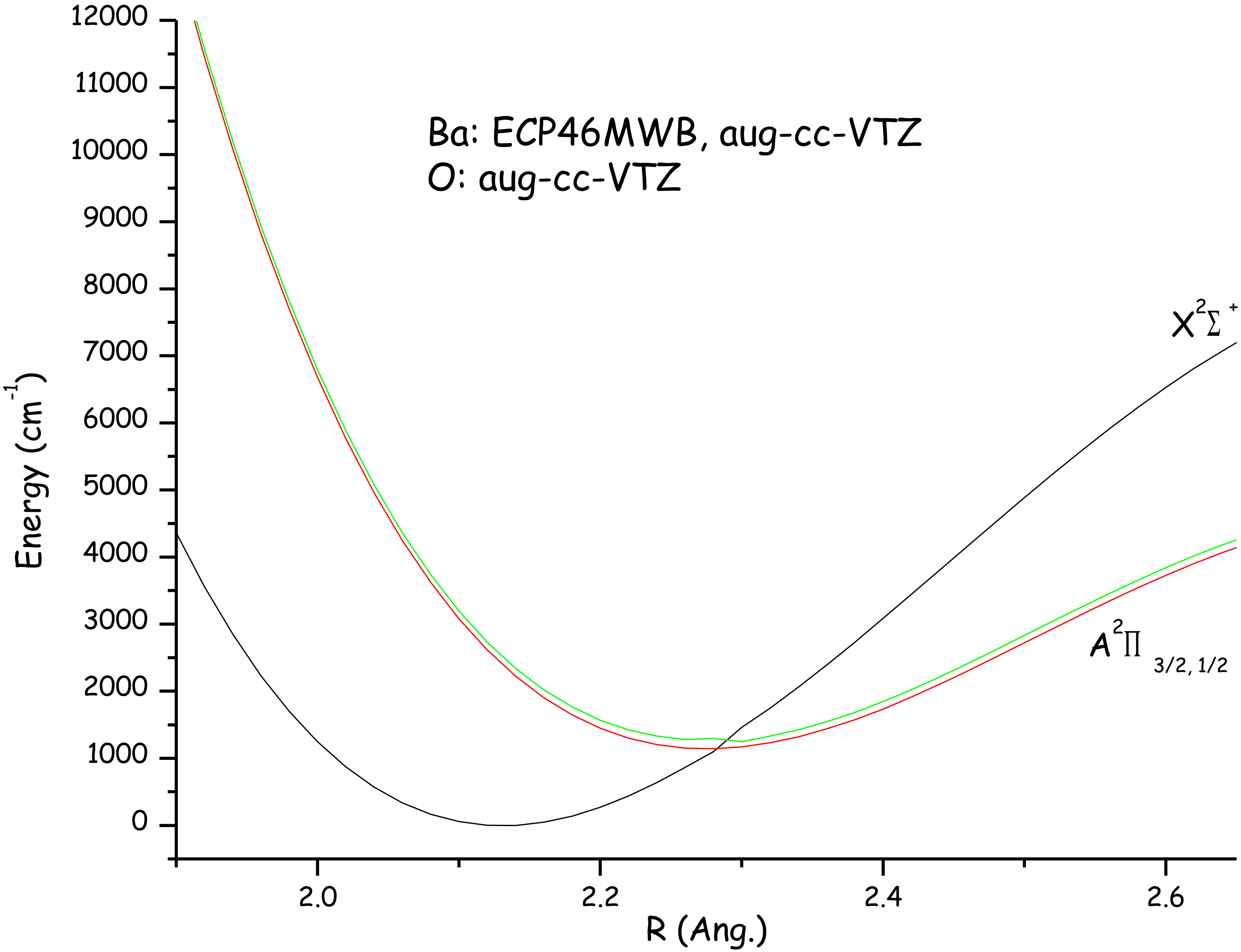
Ionizing BaO : finding the IP



ZEKEs from BaO^+

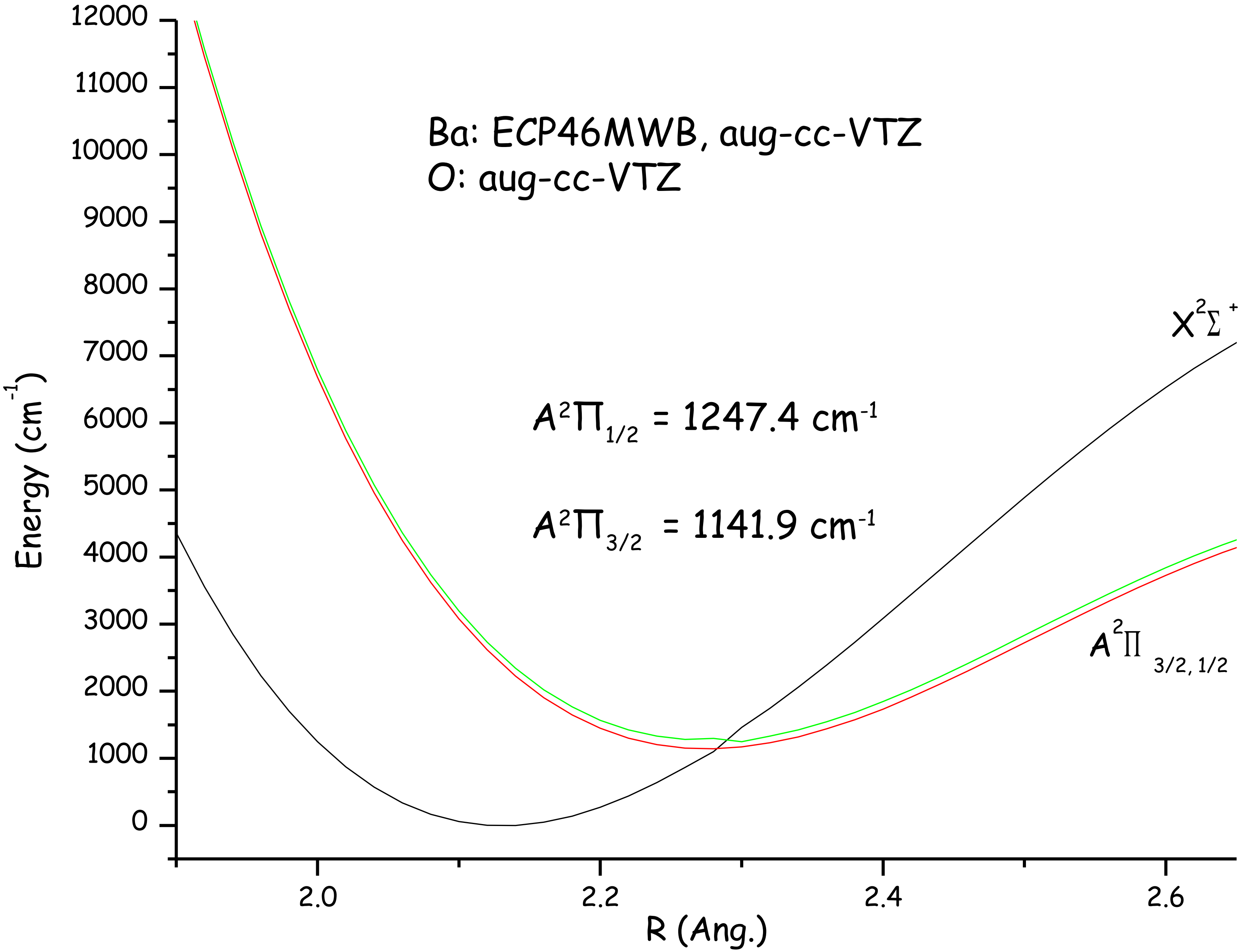


CASSCF/MRCI/SO for BaO$^+$



H-J Werner *et al.*, MOLPRO, version 2010.1

CASSCF/MRCI/SO for BaO^+



H-J Werner *et al.*, MOLPRO, version 2010.1

BaO^+ results so far

Two-photon PFI-ZEKE

$X^2\Sigma^+$		IP = 54986(3) cm^{-1}
	$\Delta G_{1/2}$	536(3) cm^{-1}

~~IP = 55600(300) cm~~$^{-1}$ [4]

4. J. Dyke *et al., J. Phys. Chem. A* (1987)

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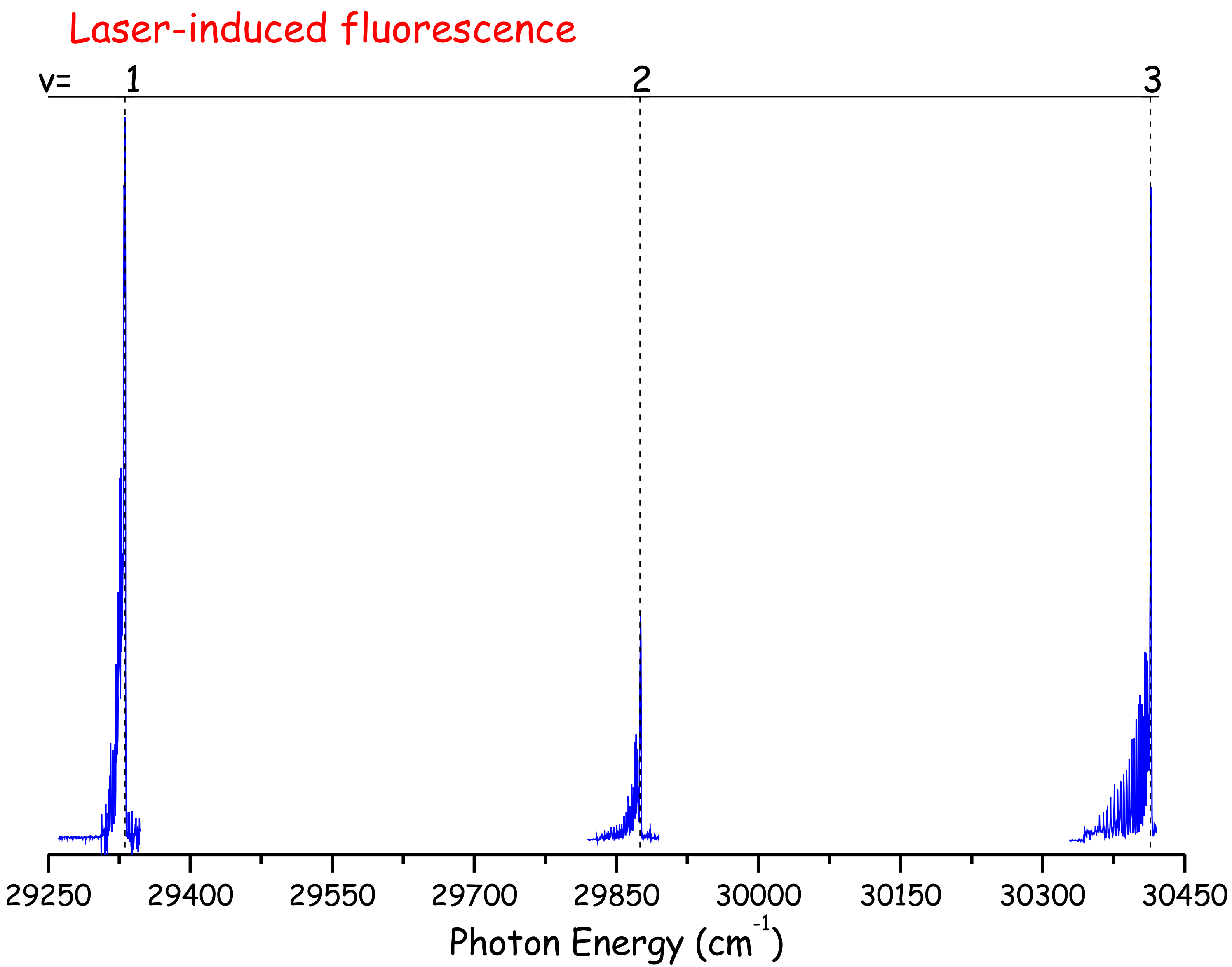
More to come...

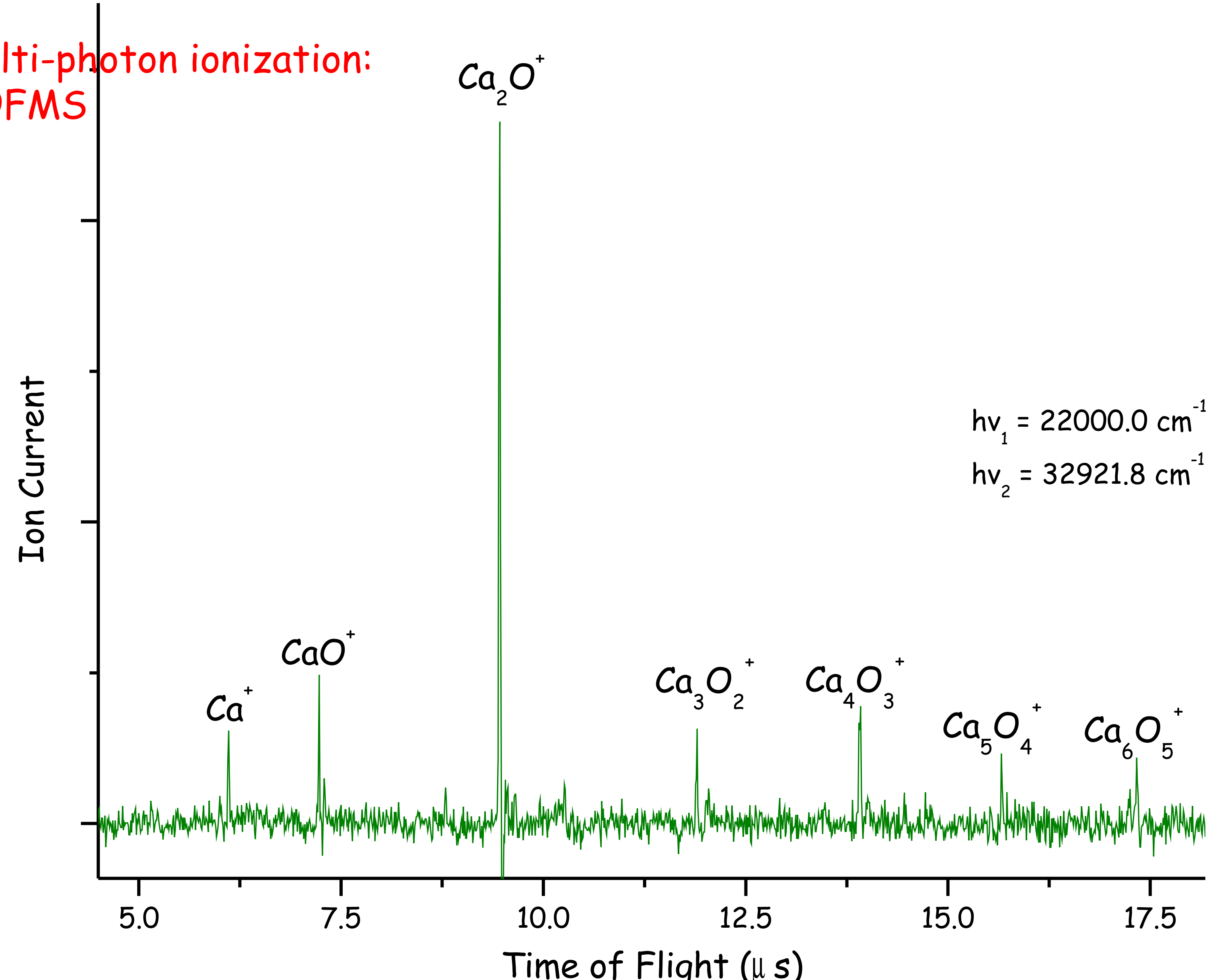
4. J. Dyke *et al.*, *J. Phys. Chem. A* (1987)

CaO $C^1\Sigma^+ \leftarrow X^1\Sigma^+$

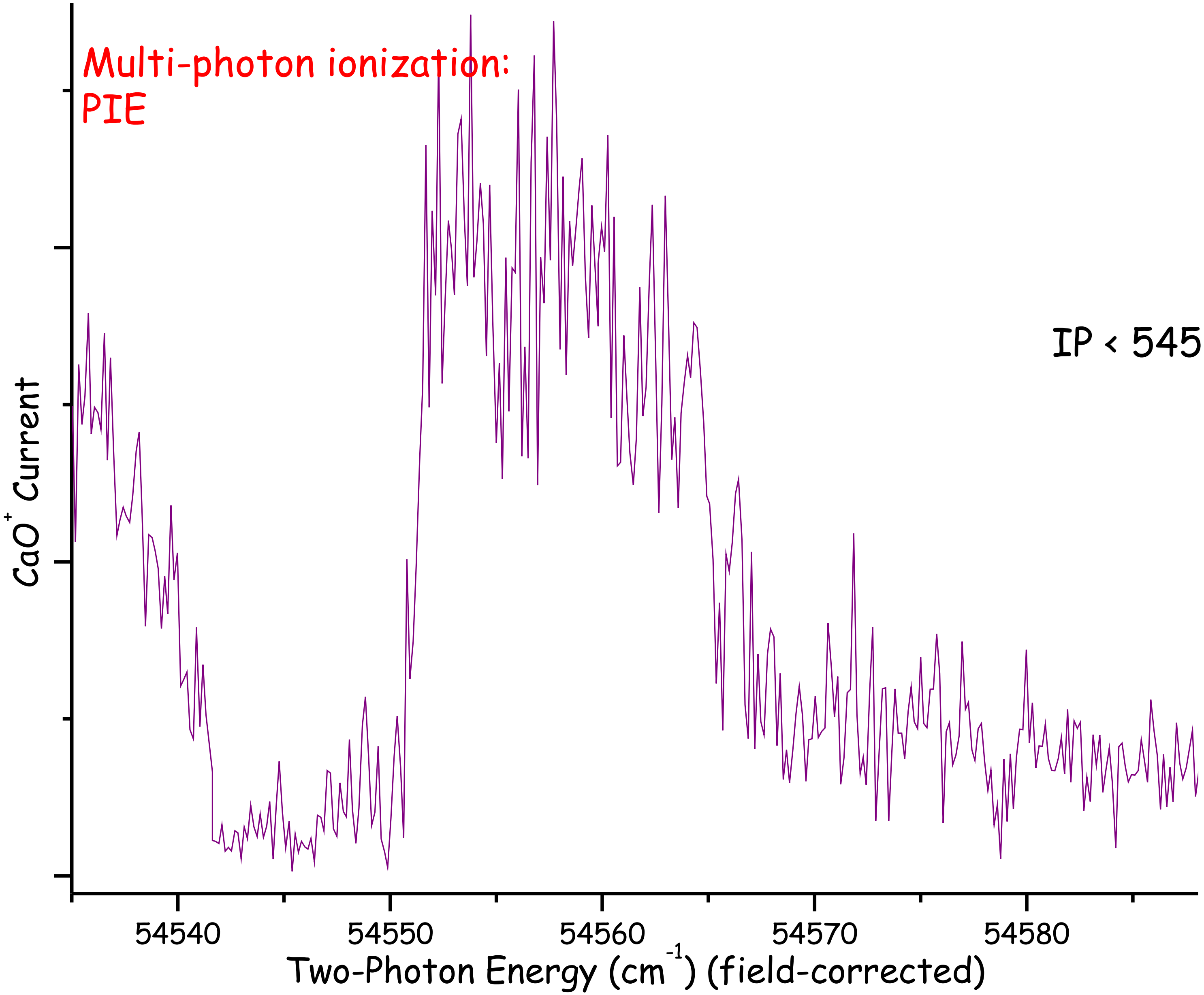


TOFMS from the CaO source

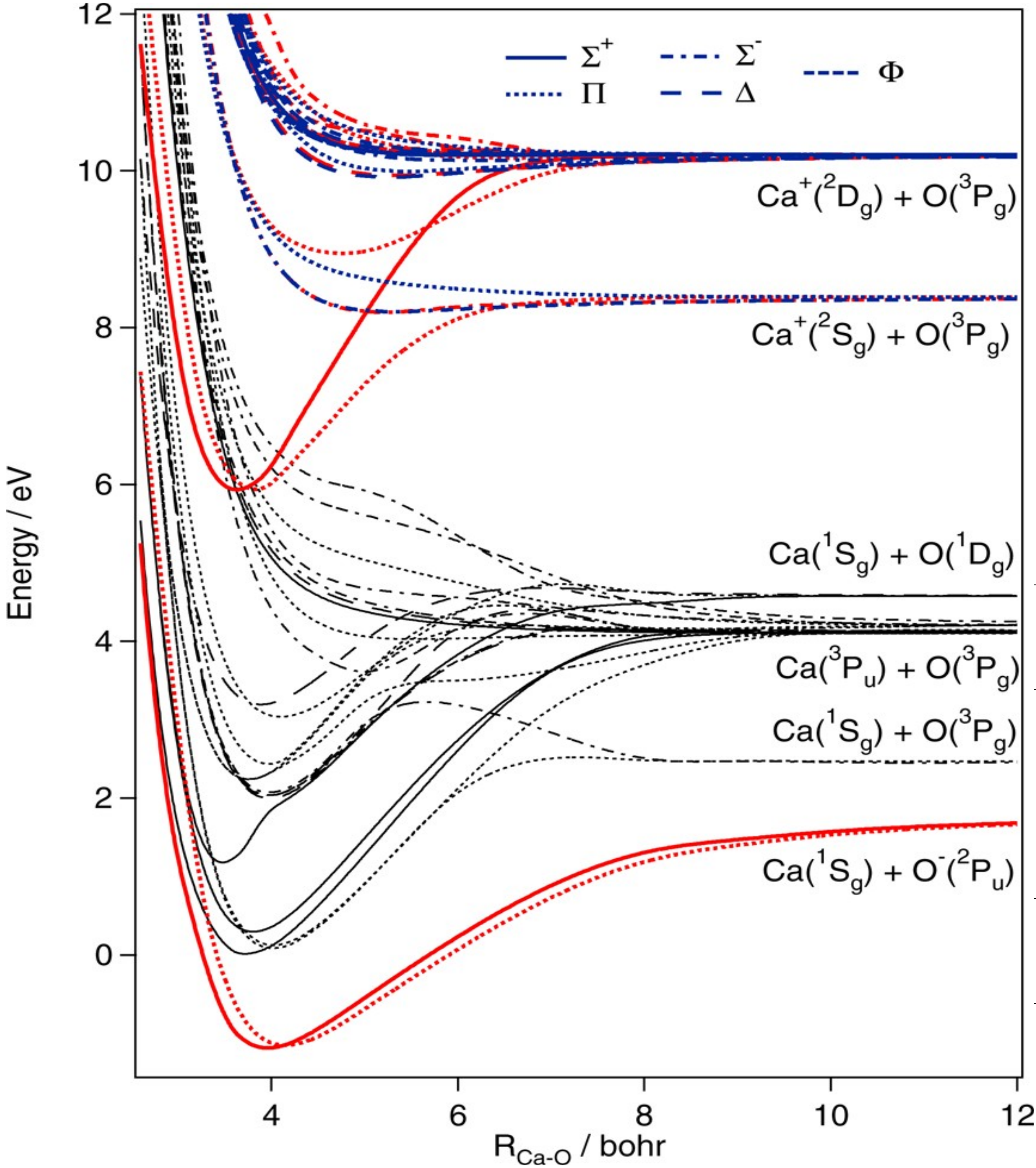
Multi-photon ionization:
TOFMS



PIE results so far with CaO



PEC for CaO^+



CASSCF potential-energy curves of the low-lying electronic
states of CaO (in black), CaO^+ (doublets are in red and quartets are in
blue), and CaO^- (doublets in red).[9]

State	Constant	Energy (cm^{-1})
$X^2\Pi$	IP	54753.7
	ω_e	639.3
	ΔE_{SO}	127.4
$A^2\Sigma^+$	T_e	564.6
	ω_e	703.2

9. H Khalil *et al., J. Phys. Chem. A* (2013)

Goals for the foreseeable future

Improve source conditions (?)

- Ablation production of CaO
- New BaO rod
- Long-term BaO production

Conclude BaO^+

- PFI-ZEKE
    - Higher energy bands (including A state)
    - Rotational resolution
- Extend theoretical work

Find CaO IP

- PIE followed by PFI-ZEKE
    - Can compare to existing theory
- Investigate Ca_nO_{n-1} production (?)

Acknowledgments

The Heaven group

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Thank you!